



Modulation of the selectivity in partial oxidation of methanol over CuZnAl catalysts by adding CO₂ and/or H₂ into the reaction feed

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ABSTRACT

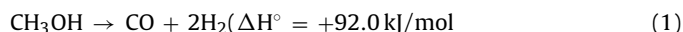
The influence of the addition of the reaction products (CO₂ and H₂) to the feed during the partial oxidation of methanol (POMeOH) was studied over a Cu/ZnO/γ-Al₂O₃ catalyst. The addition of the reaction products influences in a significantly way the selectivity to hydrogen during the reaction. The observed changes are not due to the changes suggested by the thermodynamics when promoter gases are added and might be interpreted by considering modifications in the physicochemical properties of the catalysts, particularly in the kinetic of the reactions involved in POMeOH process. In some cases CO-free hydrogen (namely highly pure, CO is not observed in analysis) could be obtained by POMeOH. The processes consider the modulation of the selectivity by a controlled amount of CO₂ and/or H₂ into the reaction flux. The presence of promoter gases strongly influenced the Cu oxidation state. It is concluded that the inhibition in CO formation is related to the high content of Cu⁰. It is suggested that in the presence of metallic copper the kinetic of the several reactions involved during POMeOH, facilitates the formation of H₂ and CO₂ and inhibits the CO formation. Results are useful for processes where the CO/H₂ ratio has to be reduced drastically (fuel cells) or finely modulated (Fischer Tropsch, methanol synthesis, etc.).

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1. Introduction

Hydrogen can be produced from partial oxidation of methanol (POMeOH) using Cu/ZnO/Al [1,2] catalysts. H₂ production from methanol may involve the following reactions [3,4]:

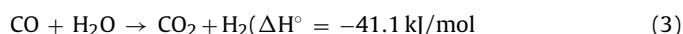
Methanol decomposition:



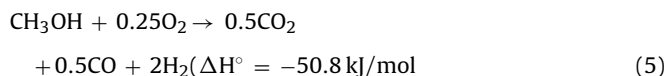
Steam reforming:



Water gas shift:



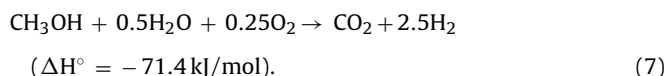
Partial oxidation:



Total oxidation:



Oxidative steam reforming of methanol:



A process for production of H₂ must fulfill several criteria, principally: i) to be clean and environmentally friendly avoiding contaminants and/or toxic emissions, ii) to be energy efficient having a low energy consumption, iii) to respond to transient behavior,

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particularly in the case of application in on-board fuel cells or industrial plants, and iv) to produce hydrogen with a high yield and a high selectivity, particularly with very low CO levels. CO is a hazardous substance which has to be produced in a controlled way. Particularly in a fuel cell, CO is a poison that deactivates the Pt-based catalyst at the anode already at concentrations exceeding a few parts per million [5,6]. It was already showed that CO formation can be controlled by stabilizing copper in metallic form on the surface. The copper metal is active for oxidation of methanol to H₂ and CO₂, whereas Cu⁺ favors the formation of H₂O and CO and Cu²⁺ as CuO shows very low activity for methanol conversion producing only CO₂ and H₂O [1]. However, the oxidation state of copper is very difficult to be controlled and often it is modulated using solid promoters or modifying the operational reaction oxidation conditions. As reported in literature, very high hydrogen yields can be achieved if the reaction is carried out at an O₂/CH₃OH ratio close to stoichiometry and temperatures exceeding 300 °C. However, the hydrogen selectivity decreases with increasing oxygen partial pressure, while the carbon dioxide selectivity increases. On the other hand, the carbon dioxide selectivity decreases with increasing temperature, when all oxygen is consumed. By running the reaction at lower temperatures, the carbon dioxide selectivity can be maintained high (almost 100%) at the cost of a lower hydrogen yield [1,2].

It is well recognized that catalysts can be modified in different ways, during catalytic reactions due to dynamic processes which occurs under reaction conditions. The number of catalytic sites and the oxidation state of the active component change during the reaction (dynamic processes) which induces changes in the catalytic performances. Thus, it is very difficult to maintain, in a controlled manner, the optimal oxidation state of the catalyst components adding metallic promoters, without modifying the operating conditions of the process. Then, it is absolutely necessary to improve the knowledge of the effects induced by these dynamic processes on the catalysts during reaction because the performance, the selectivity and the control of deactivation of a catalyst are directly related to those effects. Previously, we have shown that changing the oxidation state of the metal in catalysts leads to the modification of the kinetics of the different reactions, which are involved in the process, explaining the changes in the selectivity of the reaction. The principal objective of this work is to demonstrate that using gas promoters in the reaction feed it could be possible to obtain CO-free hydrogen under soft reaction conditions. The addition of gaseous promoters in the reaction feed is an interesting and promising new and practical approach to study processes in presence of oxygen, where the selectivity is difficult to be controlled. [7–11]. It is performed particularly modulating the oxidation state of atoms at the surface of oxides at work. The choice of H₂ and CO₂ seems to be interesting since previous studies in the partial oxidation of methane over Rh/Ti-modified catalysts put into evidence, that the addition of H₂ or CO₂ as gas promoters led to changes in the oxidation state and dispersion of rhodium [7] thus modifying the catalytic performance and the selectivity in respect to that obtained without any gas promoters in the feed. In addition it was shown that the changes induced by gas co-feeds are reversible [7], then in the case of changes in the feed composition of a process, the amount of the gas promoters can be adjusted without difficulty. An important result is that the initial levels of conversions, yields and selectivities can be restored by taking off the gas dope from the feed, facilitating the operation of reactors in which the process is actually operating. Moreover, it was demonstrated that the H₂/CO of syngas ratio can be modulated adding gas co-feed during partial oxidation of methane, which is an important founding, since it is well known that depending on the further use (Fischer Tropsch, methanol synthesis, etc.), this ratio has to be rigorously controlled [7]. In addition, one could be note that the catalytic performance

over supported metal catalysts strongly depends on the reaction conditions.

The oxidation state of the active metal during the reaction plays a crucial role. More oxidizing atmosphere in the presence of CO₂ and more reducing atmosphere in the presence of H₂ or CO modify the catalytic properties of the active phase. In the case of the H₂, CO and CO₂ dopes, results suggested that during the methanol oxidation reaction the products of the reaction could influence significantly the activity and the distribution of the products [9].

Recently, some papers were published taking into account the role of the oxidation states of Cu on the relation between product distribution and catalytic state [12,13]. In those studies, the mechanisms of methanol decomposition, methanol oxidation and methanol steam reforming on a CuO (1 1 1) surface have been investigated by using density functional theory calculations and self-consistent periodic calculation at the molecular level. The calculations demonstrate that the specific structure of oxygen on CuO (1 1 1) plays an important role in the formation of CH₃O. Comparing with clean CuO (1 1 1) surface, the introduction of oxygen atom reduces the activation barrier of OH bond-cleavage respect to the CO bond cleavage, which indicated that the OH bond cleavage on the oxygen-precovered CuO (1 1 1) surface is the most possible pathway. This indicating, that oxygen acts as a promoter for the formation of CH₃O by CH₃OH decomposition on oxygen-precovered CuO (1 1 1) surface.

The present work reports new results obtained by co-feeding of H₂, CO₂ and H₂ + CO₂ in the feed (methanol, O₂) in the partial oxidation of methanol (POMeOH) over a Cu/ZnO/γ-Al₂O₃ catalyst. It seems that for the first time it will be shown that the addition of gas promoters changes the performance and the selectivity of the catalyst observed in standard POMeOH conditions (without co-feeds), confirming that dynamic processes are taking place over the catalyst. It will be demonstrated that modulating the composition of the reaction feed, CO-free hydrogen under soft reaction conditions can be obtained. Preliminary explanations based on the comparison of the results with thermodynamic predictions and catalyst characterizations are proposed. The results can be useful for the selective partial oxidation of methanol processes where a very small amount of CO (or a very little CO/H₂ ratio) is necessary to be finely controlled. Results are also useful for the knowledge of the influence of the products of the reaction in the POMeOH process.

2. Experimental

2.1. Catalyst preparation

CuZnAl-hydrotalcite-like hydroxycarbonate precursors with Cu:Zn:Al = 2:2:1 atomic ratio was synthesized by a coprecipitation method at room temperature by reacting aqueous solutions containing a mixture of Cu(NO₃)₂·2.5H₂O (Riedel de Haën, 99.99%), Zn(NO₃)₂·6H₂O (Fluka, 99.99%) and Al(NO₃)₃·9H₂O (Panreac, PRS 99.98%) salts and a mixture of NaOH (≈2 M solution, Panreac, pa) and Na₂CO₃ (≈0.3 M solution, Panreac PRS 99%) at a constant pH (≈9). The resulting precipitate was aged at 65 °C for 30 min under stirring in a magnetic stirrer, filtered, washed with deionized water several times until the pH of the filtrate was 7 and then dried in an air oven at 70 °C overnight. The resulting powder was calcined in a furnace under air at 450 °C for 5 h. The theoretical relative weight percentage of each metal in the solid was 40% Cu, 49% Zn and 11% Al, (catalyst named as Cu₄₀Zn₄₉Al₁₁).

2.2. Characterization techniques

Catalysts characterizations were made over the fresh (obtained following preparation protocol as described above), pre-treated

and after the catalytic test samples using N₂ adsorption (BET), X-ray diffraction and X-ray photoelectron spectroscopy (XPS).

2.2.1. N₂ adsorption

The specific surface area of the samples was calculated from N₂ (Indugas, 99.995%) adsorption experiments using the Brunauer, Emmett and Teller (BET) method. The instrument used was a multi-point Micromeritics TriStar (3000). Prior to the analysis, samples (0.2 g) were outgassed at 150 °C under a 0.13 Pa vacuum.

2.2.2. X-ray diffraction

The samples were analyzed by X-Ray diffraction (XRD) using a Siemens D5000 diffractometer (CuK α radiation, $\lambda = 0.15418$ nm), in the range $2\theta = 10$ – 70° at room temperature. Lines were attributed using a DIFFRAC-AT software.

2.2.3. X-ray photoelectron spectroscopy (XPS)

XPS was performed with a SSI X-probe (SSX-100/206) spectrometer from Surface Science Instrument (Fisons) working with a monochromatic Al K α radiation (10 kV, 22 mA). Charge neutralization was achieved by using an electron flood gun adjusted at 8 eV and placing a nickel grid 3.0 mm above the sample. Pass energy for the analyser was 50 eV and the spot size was 1000 nm in diameter, corresponding to a full width at half maximum (FWHM) of 1.1 eV for the Au 4f_{7/2} band of a gold standard. For these measurements, Cu 2p, Zn 2p, O 1s and C 1s bands were recorded.

Samples were reduced “ex-situ” in H₂ before XPS analysis. In the standard XPS analysis the samples were outgassed overnight under vacuum (10^{-5} Pa) and then introduced into the analysis chamber where the pressure was around 10^{-7} Pa. In both cases, the binding energies were calibrated by fixing the C–(C, H) contribution of the C 1s adventitious carbon at 284.8 eV. Peaks were considered to be combinations of Gaussian and Lorentzian functions in an 85/15 ratio, working with a Shirley baseline, for the measurements with the SSI, and in a 70/30 ratio, working with linear baseline, for those with the Kratos (following recommendations from the supplier). For the quantification of the elements, sensibility factors provided by the manufacturers were used. Decomposition of the Cu 2p doublets was done by fixing an energy gap of 19.9 eV, and an area ratio of 1/2 between the Cu or Zn 2p_{3/2} and the 2p_{1/2} bands, in accordance with the values reported for Cu or Zn elsewhere [14]. During XPS analysis we have not registered the KLM Auger spectra.

2.3. Catalytic test

Pretreatment of the catalysts:

Prior to the POMEH tests, CuZnAl catalyst was reduced in situ under a pure H₂ (Proxair, 99.9%) flow ($100 \text{ cm}^3 \cdot \text{min}^{-1}$) at 300 °C for 2 h and then cooled to 150 °C using a heating ramp of $10^\circ\text{C} \cdot \text{min}^{-1}$.

2.3.1. Catalytic activity measurements

Catalytic tests were performed in a fixed-bed micro reactor of 1 cm inner diameter (PID ENG&Tech, Spain). The total flow was 100 ml/min over 100 mg of powdered catalyst (granulometry 200–315 μm) dispersed in 600 mg of quartz bills (500 μm). After pretreatment of the catalyst as indicated above, methanol conversion was measured every 50 °C in a stepwise way with a staying time of 45 min at each temperature in order to allow 4 analyses of the reactor gaseous outlet from 150 to 350 °C. Analysis of reactants and products was performed by on-line gas chromatography (Varian CP3800) during the whole catalytic test. The detection and quantification of compounds were performed in a thermal conductivity (TCD) detector operating at a programmed temperature. CP-PoraPLOT Q (25 m; 0.53 mm) and CP-Molsieve 5 Å (25 m; 0.53 mm) columns were used for the separation of the reaction products. The detection limit for CO, H₂ and CO₂ was 100 ppm.

The following molecules were analyzed during the reaction: H₂, O₂, CH₄, CO, CO₂, methanol, methyl formate, and H₂O. Any presence of formaldehyde and formic acid was detected. Response factors of detector were determined by injection of different gas mixtures of known concentrations.

2.3.2. Tests in the absence of gaseous co-feeds (standard POMEH)

The reactants mixture was composed of 5 vol% CH₃OH (Merck > 99%), 2.5 vol% O₂ (Indugas 99.995%) and 92.5 vol% He (Proxair 99.99%). The methanol was introduced into the feed by the passage of a stream of He through the methanol placed in a saturator at 5.4 °C.

2.3.3. Tests in the presence of gaseous co-feeds

Two types of test were performed: i) adding a single promoter gas as H₂ (Proxair 99.995%) or CO₂ (Proxair 99.9%) as co-feed at a concentration of 5 vol% or ii) a mixture of gaseous promoters (5 vol% CO₂ + 5 vol% H₂). In all cases, the space velocity was maintained constant by balancing with He (total flow always equal to 100 ml/min).

2.3.4. Expression of the catalytic data

The catalytic activity was evaluated in terms of the conversion of methanol, which is expressed by:

$$\text{MeOH}(\%) = (\text{m}(\text{MeOH})_i - \text{m}(\text{MeOH})_f) / \text{m}(\text{MeOH})_i$$

where, i and f are respectively the initial and final amount of methanol.

The yields of H₂, CO or CO₂ produced during the reaction were evaluated by the expression:

$$Y(\%) = (\text{mXF} / \text{m}(\text{MeOH})_i) \times (\text{XF} / \text{FMeOH}) \times 100\%,$$

where, XF and FMeOH are the sensitivity factors of the product (X) and methanol (MeOH), respectively.

In the case that the reaction products were added in the feed, the yields were calculated by performing the difference between the measured and introduced amounts. The selectivity of the reaction products was determined by:

$$S_i = n_i c_i / \sum n_i c_i$$

where n_i is the number of carbon atoms in the product i and C_i is the concentration of product i .

2.3.5. Thermodynamic calculations

Thermodynamic calculations for the conditions used in this study were performed to determine the equilibrium levels that can be predicted when co-feeds are added using Outokumpu HSC Thermodynamic Software. These thermochemical calculations are based on enthalpy, entropy and heat capacity or Gibbs energy values for the chemical species [15]. The program used calculates the amounts of products at equilibrium in isothermal and isobaric conditions. The substances to be taken into account in the calculations, the amount of reactants, the potentially stable phases (gas phase) as well as the temperature of raw materials were specified as input. In the calculations the following substances in the gas phase were considered: CH₃OH, O₂, N₂, CO, H₂, CO₂ and H₂O. Calculations were performed at atmospheric pressure and in the 100–400 °C temperatures range. For the standard POMEH calculations, the feed was composed of 5 vol% of CH₃OH and 2.5 vol% O₂ diluted in N₂. For the calculations performed in the presence of co-feeds, the feed consisted of CH₃OH, (5 vol%), O₂ (2.5 vol%), the gaseous co-fed (5 vol% of H₂, 5 vol% of CO₂ or 5 vol% CO₂ + 5 vol% H₂) diluted in N₂. The activity coefficient of species in the gas mixture was selected as unity (Raoultian activity). The equilibrium composition

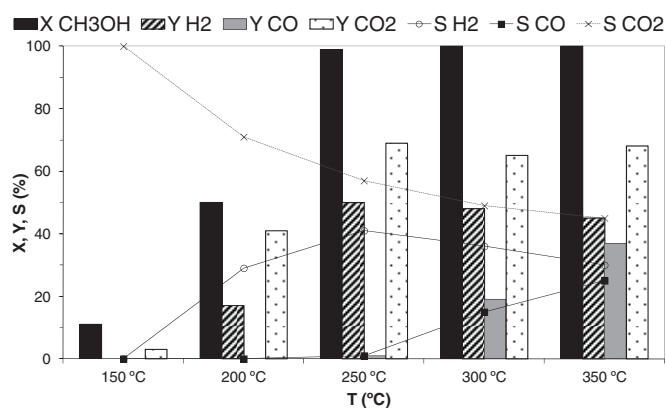


Fig. 1. Conversion, yield and selectivity in POMeOH reaction (Standard test: 5 vol % CH₃OH, 2.5 vol% O₂ and 92.5 vol% N₂) measured over Cu/ZnO/Al₂O₃ as a function of temperature.

was calculated by the Gibbs energy minimization method, which takes into account the different reactions and gaseous species that could be involved in the different sets of reaction conditions considered and introduced as starting data. The GIBBS program finds the most stable phase combination and seeks the phase composition where the Gibbs energy for the system reaches its minimum at constant pressure and temperature.

3. Results and discussion

3.1. Catalytic activity

3.1.1. Test in the absence of gaseous co-feeds (Standard POMeOH test)

3.1.1.1. Catalytic performances. Fig. 1 shows the evolution of the catalytic performance for standard POMeOH over Cu/ZnO/Al₂O₃ with temperature (between 150 °C and 350 °C). As expected the methanol conversion increases as a function of temperature. The yields toward the products of the partial oxidation of methanol (H₂ and CO₂) also increased with temperature up to 250 °C, then slightly decreasing with increasing temperature up to 350 °C. The behavior of the selectivity to H₂ is similar to the yield while the selectivity to CO₂ decreases significantly with the temperature.

3.1.1.2. H₂/CO and the H₂/CO₂ ratios. Table 1 shows the H₂/CO and the H₂/CO₂ ratios at 250 °C and 350 °C. Both ratios vary with the reaction temperature. At low temperatures (<250 °C), yields and selectivities to H₂ are much lower than CO₂ (H₂/CO₂ = 0.42 at 200 °C), whereas this ratio increases at higher temperatures, reaching a value close to 0.7 at 250 °C. Still, the relationship H₂/CO₂ is far from that expected for a stoichiometric POMeOH (H₂/CO₂ = 2, Reaction (1)). No formation of CO is detected below 250 °C while a low production is observed at 250 °C (1%). Moreover, from 300 °C it is observed an increase in the CO production (to 37% at 350 °C). The H₂/CO is very high (30) at 250 °C and drops sharply to 1.3 at 350 °C.

Table 1

H₂/CO and H₂/CO₂ molar ratios in POMeOH conditions at 250 °C and 350 °C in absence or presence of gas co-feedings. In parenthesis, H₂/CO molar ratio thermodynamically calculated.

	H ₂ /CO		H ₂ /CO ₂	
	250 °C	350 °C	250 °C	350 °C
POMeOH	30 (6.3)	1.3 (3.5)	0.7	0.7
POMeOH + 5% H ₂	No observed (0.4)	1.7 (2.8)	1.2	0.8
POMeOH + 5% CO ₂	7 (4.9)	2.2 (2.4)	1.3	1.2
POMeOH + 5% H ₂ + 5% CO ₂	No observed (3.8)	No observed (1.8)	1.3	2.2

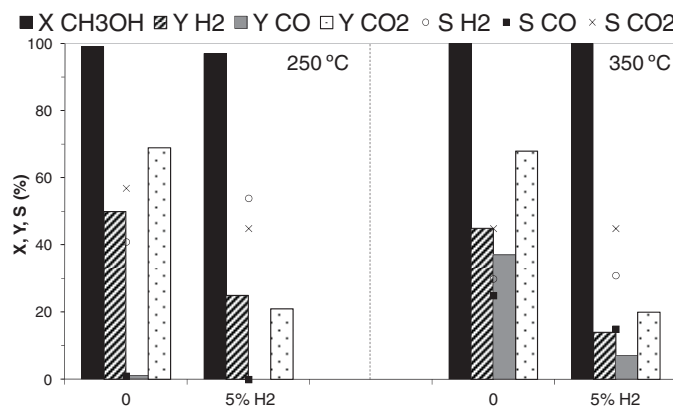


Fig. 2. Conversion, yield and selectivity in POMeOH reaction in the presence of H₂ as co-feed at 250 and 350 °C (5 vol % CH₃OH, 2.5 vol% O₂, 5 vol % H₂ and balanced with N₂ till 100 ml/min) at 250 and 350 °C.

These results confirm that other reactions are carried out under the experimental conditions used in this work. The reverse water gas shift reaction (Reaction (3)) could take place simultaneously with POMeOH reaction (Reaction (4)), thus increasing the RWGS products (CO and H₂O, this latter product is not shown in Fig. 1).

3.1.2. Tests in the presence of gaseous co-feeds

3.1.2.1. Effect of the reaction temperature on the reaction products.

Two temperatures (250 °C and 350 °C) were selected to study the effect of gaseous promoters on methanol conversion, hydrogen and CO₂ yields and selectivities. Both temperatures were chosen considering that at 250 °C the CO production is minimal (1%) increasing up to 37% at 350 °C for the standard POMeOH.

3.1.2.2. Catalytic activity in presence of gaseous promoters.

3.1.2.2.1. -H₂ as co-feed. Fig. 2 illustrates the influence of the addition of 5% of H₂ to the feed at 250 °C and 350 °C. Comparing with the results obtained in the absence of H₂ (standard POMeOH test), the following effects are observed:

Conversion is practically not affected by the addition of H₂ to the feed. Nevertheless, it negatively affects the yield to H₂ and CO₂ that shows a strong decrease. However, an increase in the selectivity to H₂ and a decrease in the CO₂ selectivity were observed at 250 °C while both remains practically constant at 350 °C. CO is not observed at 250 °C and it shows a significant decrease at 350 °C.

3.1.2.2.2. -CO₂ as co-feed. Fig. 3 shows the influence of adding CO₂ (5%) to the feed at 250 °C and 350 °C on the catalytic performance. The following effects are observed in reference to the results obtained in the absence of CO₂:

Conversion remains unchanged in the presence of CO₂ in the feed. The co-feeding of CO₂ causes a decrease in the yield to H₂ and CO₂. However, the selectivity to H₂ increases at both temperatures in the presence of CO₂ while the selectivity to CO₂ decreases at both temperatures. The CO yield increases first (250 °C) and then decreases while increasing the reaction temperature.

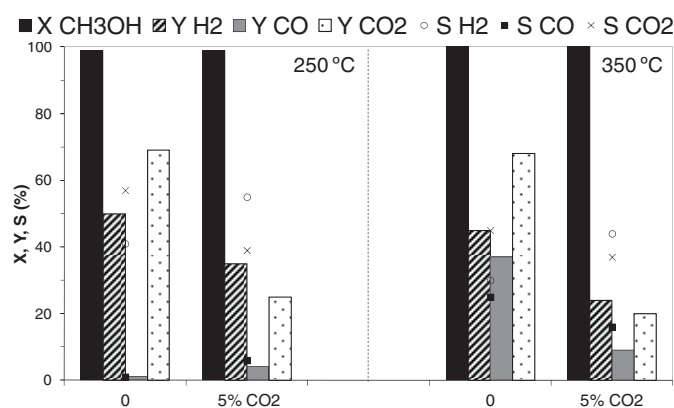


Fig. 3. Conversion, yield and selectivity in POME OH reaction in the presence of CO₂ as co-feed at 250 and 350 °C (5 vol% CH₃OH, 2.5 vol% O₂, 5 vol% CO₂ and balanced with N₂ till 100 ml/min) at 250 and 350 °C.

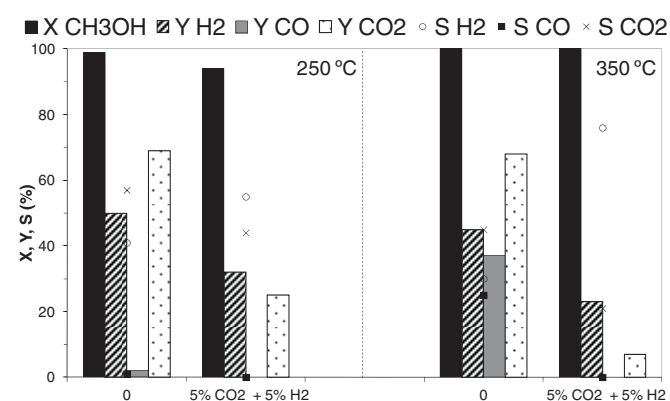


Fig. 4. Conversion, yield and selectivity in POME OH reaction in the presence of 5 vol.% CO₂ + 5 vol.% H₂ as co-feed at 250 and 350 °C (5 vol% CH₃OH, 2.5 vol% O₂, 5 vol% H₂, 5 vol% CO₂ and balanced with N₂ till 100 ml/min) at 250 and 350 °C.

3.1.2.2.3. -CO₂ + H₂ as co-feed. The results obtained when adding simultaneously 5% CO₂ + 5% H₂ to the feed are shown in Fig. 4. The following effects are observed respect to the results obtained in the absence of gas promoters: The conversion slightly decreases at 250 °C. The yield to H₂ and CO₂ decreases progressively as the reaction temperature increases from 250 °C to 350 °C. The H₂ selectivity increases while the CO₂ selectivity decreases with the reaction temperature. An important observation was stated. The co-feeding of H₂ + CO₂ decreases drastically (CO is not observed) the production of CO at both temperatures. In addition the CO₂ yield decreases significantly, principally at 350 °C.

3.1.2.2.4. The H₂/CO ratio. A particular interest is to study the evolution of the H₂/CO ratio as function of the temperature when the gaseous co-feeds were added (Table 1). The H₂/CO ratio decreases in the presence of 5% of CO₂ or becomes very high (CO is not observed) in the presence of 5% H₂ or 5% H₂ + 5% CO₂ at 250 °C. This ratio slightly increases at 350 °C when 5% CO₂ or 5% H₂ are co-fed (from 1.3 to 1.7 or 2.2, respectively).

3.2. Thermodynamic calculations

Figs. 5 and 6 give the thermodynamic equilibrium results calculated for the standard POME OH and for the addition of 5 vol% of H₂, CO₂ or 5 vol% CO₂ + 5 vol% H₂ to the POME OH feed and the experimental catalytic results obtained in similar reaction conditions at 250 °C and 350 °C, respectively.

Comparing both values, the following trends are observed at 250 °C:

3.2.1. Addition of 5 vol% of H₂ as co-feeds

When adding H₂ (5 vol%), H₂ selectivity increases whereas a strong decrease is predicted by thermodynamic. The CO₂ selectivity decreases but not as strongly as predicted by thermodynamic. No production of CO is detected while a significant increase is predicted.

3.2.2. Addition of 5 vol% of CO₂ as co-feeds

In the presence of CO₂ (5 vol%), H₂ selectivity value showed a moderately increase while a weak decrease is thermodynamically expected. Practically no change is detected for CO selectivities trends. However a significant decrease of the CO₂ selectivity is observed compared to that calculated by thermodynamic.

3.2.3. Addition of 5 vol% H₂ + 5 vol% CO₂ as co-feeds

Concerning 5 vol% H₂ + 5 vol% CO₂ co-feeds, the tendency for H₂ selectivity is similar to that observed in presence of CO₂ co-feed. No change is observed for CO₂ selectivity trends. No production of CO is experimentally detected while it should increase according to thermodynamic calculations.

The following trends are observed at 350 °C:

-in the presence of H₂ (5 vol%), H₂ and CO₂ selectivities are approximately constant while a weak decrease is predicted. CO selectivity decreases as an increase is predicted by calculations.

-when adding CO₂ (5 vol%), H₂ selectivity is greatly increased while the calculations predict a value approximately constant. The selectivity to CO₂ and CO decrease and this is not consistent with the results predicted by thermodynamics.

-in the presence of 5 vol% H₂ + 5 vol% CO₂, H₂ selectivity shows a strong increase while a significant decrease is predicted. No change is observed for CO₂ selectivity trends. No production of CO is detected while it should strongly increase according to thermodynamic calculations.

3.2.4. The H₂/CO ratios

H₂/CO ratios predicted by thermodynamics calculation (Table 1) show a decrease in the presence of gaseous co-feeds at both temperatures, i.e., an increase in the CO production. However, the experimental data show the opposite trend for this ratio (i.e., a reduction in CO production (except for the POME OH + 5% CO₂)).

As a conclusion the comparison between the experimental catalytic and thermodynamic predicted trends shows significant discrepancies at both temperatures, indicating, as expected, that the changes observed are due to kinetics modification due to the addition of gas promoters in the reactant gas feed.

3.3. Catalyst characterization

3.3.1. XRD analysis

3.3.1.1. Fresh and spent CuZnAl catalysts after standard conditions.

Fig. 7 shows XRD patterns obtained for both fresh and spent CuZnAl catalysts. Pretreatment of the fresh catalyst under the hydrogen atmosphere at 350 °C, causes the reduction of Cu^{II} to Cu⁰ and Cu^I (Fig. 7a). The reduced copper was also detected in the catalyst after the catalytic test in standard conditions principally at 350 °C (Fig. 7c). Part of the Cu⁰ is oxidized to Cu^I, as evidenced by the appearance of the peak corresponding to Cu₂O phase principally at 250 °C and 350 °C. Small peaks corresponding to the CuAl₂O₄ spinel phase were observed.

3.3.1.2. CuZnAl catalysts in presence of gas co-feeds. In the presence of gas co-feeds (5 vol% H₂, 5 vol% H₂ + 5 vol% CO₂ or 5 vol% CO₂) (Figs. 7b and c), the relative amount of Cu⁰ and Cu^I varies according to the reaction temperature. Thus, the copper after the catalytic test at 250 °C is almost oxidized to Cu^I (intense band corresponding to Cu₂O (Fig. 7b)), whereas after the catalytic test at 350 °C

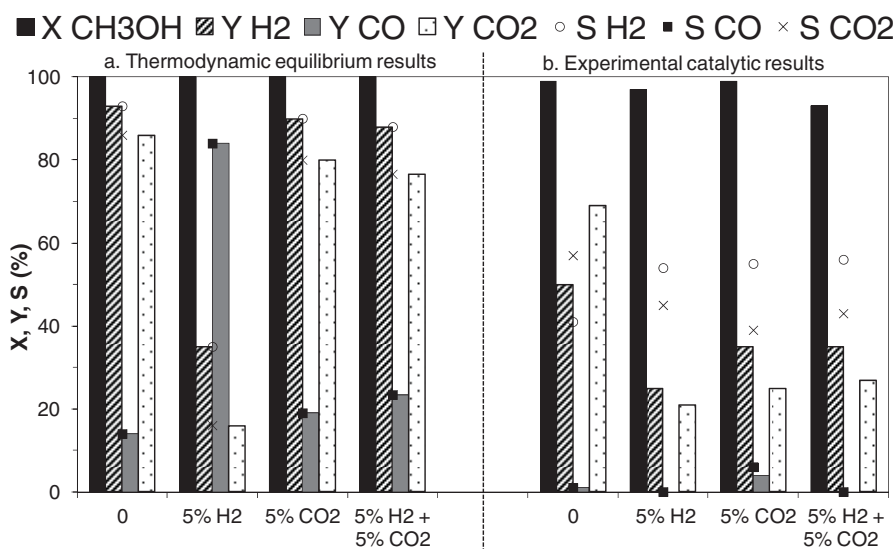


Fig. 5. POME OH reaction at 250 °C. a) Thermodynamic equilibrium and b) experimental catalytic results in the presence of different co-feeds (5 vol% H₂, 5 vol% CO₂ and 5 vol% H₂ + 5 vol% CO₂).

(Fig. 7c) the majority phase is that corresponding to Cu⁰. Moreover, some very small peaks corresponding to the CuAl₂O₄ spinel phase could be seen at 2θ about 32, 59, 67° [16]. These peaks were not observed after test at 250 °C. No peak attributed to ZnO phase was observed.

3.3.2. XPS analysis

XPS atomic ratios and the Cu 2p_{3/2} binding energies for all samples are shown in Tables 2–4. The presence of carbon was detected over all samples but the surface C contamination was low and stable among the various samples, thus indicating that there was no preferential coke deposition on the surface of the catalyst during the tests. No other contaminants were observed (Na, Cl ions) on the materials surface.

3.3.2.1. Comparison between spent CuZnAl catalysts after standard conditions and in presence of gaseous dopes.

3.3.2.1.1. Cu⁰+Cu⁺/(Zn + Al) atomic ratio values. The dispersion of copper significantly increases after the reduction pretreatment (in respect to the value observed for the fresh sample) as evidenced by the increase of the XPS Cu⁰+Cu⁺/(Zn+Al) atomic

ratio (0.80 vs 0.42, Table 2). XPS Cu⁰+Cu⁺/(Zn+Al) atomic ratio values observed for the samples after the catalytic tests at 250 °C, in the different reaction atmospheres, are nearly similar (0.80–0.84) to the values measured for the pre-reduced sample and for the sample after standard POME OH (0.80 and 0.75, respectively), except for the sample after POME OH + 5 vol CO₂% for which a decrease in this ratio is observed. As compared to standard POME OH, the molar concentration of Cu⁰+Cu⁺ increased weakly (from 6.03 after standard POME OH to 7.85, 8.01 and 8.26 after the tests in the presence of dopes). At 350 °C, the XPS Cu⁰+Cu⁺/(Zn+Al) atomic ratio increased from 0.83 to 1.19 after POME OH with dopes. As shown in Table 2 and Table 3 incorporation of CO₂ and H₂ dopes into the reactant gas mixture increases the overall reduction of Cu. Indeed, as compared to standard POME OH test the molar concentration of Cu⁰+Cu⁺ increased from 7.95 to values of 8.45, and from 11.42 to 12.06 after the tests with different dopes.

3.3.2.1.2. Binding energies of Cu 2p_{3/2}. The binding energies of Cu 2p_{3/2} over the fresh, reduced and after catalytic tests of all catalyst are shown in Table 4. Binding energies values seems to be independent of the type of test. They are similar for used

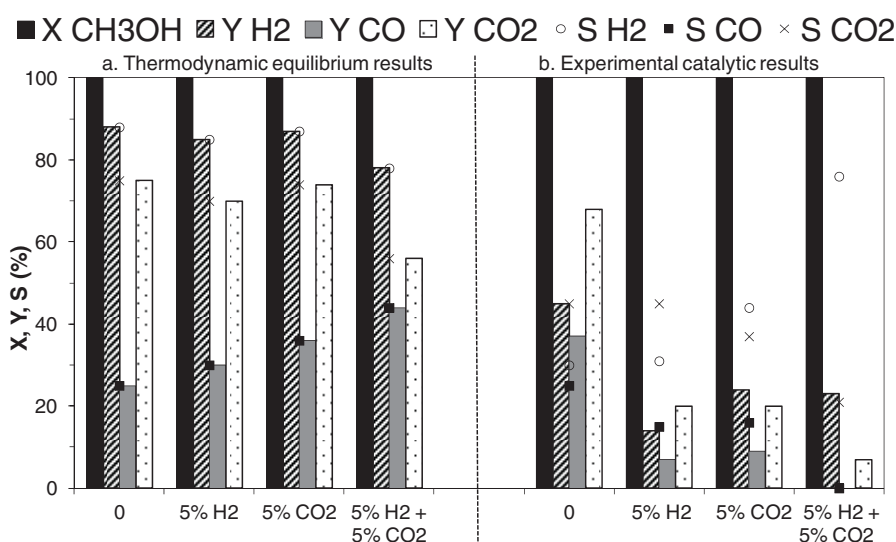


Fig. 6. POME OH reaction at 350 °C. a) Thermodynamic equilibrium and b) experimental catalytic results in the presence of different co-feeds (5 vol% H₂, 5 vol% CO₂ and 5 vol% H₂ + 5 vol% CO₂).

Table 2

Summary of XPS data obtained over CuZnAl for the fresh, reduced and spent catalysts at 250 and 350 °C in absence or presence of co-feedings.

CuZnAl	Cu ^{0/+} /(Zn + Al)		C/(Zn + Al)		Cu ²⁺ /(Cu ⁺ + Cu ⁰)	
	250 °C	350 °C	250 °C	350 °C	250 °C	350 °C
Calcined		0.42		0.81		0.05
Reduced		0.80		0.90		0.15
POMeOH	0.75	0.81	0.77	0.88	0.17	0.34
POMeOH + 5% H ₂	0.80	0.90	0.60	0.91	0.08	0.17
POMeOH + 5% CO ₂	0.68	0.83	0.93	0.95	0.20	0.13
POMeOH + 5% H ₂ + 5% CO ₂	0.84	1.19	0.99	0.77	0.22	0.27

Table 3

Summary of XPS data obtained over CuZnAl for spent catalysts at 250 and 350 °C in absence or presence of co-feedings. Molar concentration and XPS ratio are calculated from Cu 2p region.

CuZnAl	Cu ⁰ + Cu ⁺		Cu ²⁺ (CuO)		Cu ²⁺ (CuAl ₂ O ₄)		Cu ^{0/+} /Cu _{Total}	
	250 °C	350 °C	250 °C	350 °C	250 °C	350 °C	250 °C	350 °C
POMeOH	6.03	7.95	2.37	1.93	0.25	0.72	0.56	0.70
POMeOH + 5% H ₂	7.85	8.45	2.48	1.67	0.35	0.53	0.65	0.79
POMeOH + 5% CO ₂	8.01	11.42	2.44	1.56	0.41	0.49	0.78	0.85
POMeOH + 5% H ₂ + 5% CO ₂	8.26	12.06	1.47	3.55	0.56	1.23	0.80	0.72

Table 4

Binding energies for calcined, reduced and spent catalysts at 250 °C and 350 °C in absence or presence of co-feedings.

CuZnAl	BE Cu 2p _{3/2} (Cu ⁰ + Cu ⁺) eV		BE Cu 2p _{3/2} (Cu ²⁺ in CuO) eV		BE Cu 2p _{3/2} (Cu ²⁺ in CuAl ₂ O ₄) eV	
	250 °C	350 °C	250 °C	350 °C	250 °C	350 °C
Calcined		932.2		933.8		936.9
Reduced		932.2		934.5		936.3
POMeOH	932.2	932.2	934.8	934.9	936.2	936.2
POMeOH + 5% H ₂	932.2	932.2	935.0	934.5	936.6	936.6
POMeOH + 5% CO ₂	932.2	932.1	934.8	934.2	936.2	936.3
POMeOH + 5% H ₂ + 5% CO ₂	932.1	932.1	934.8	934.2	936.2	936.3

catalysts after standard and after adding gas promoters in the feed, at 250 °C and 350 °C. Oxidized copper (Cu²⁺) is detected on all catalyst (Figs. 8 and 9). Moreover, contribution from CuAl₂O₄ spinel phase was observed in all XPS spectra (Fig. 9 a–d). In the case of spent catalysts (Figs. 8 and 9), Cu 2p region showed an asymmetric peak that can be decomposed in two components at 932.2 eV which could be assigned to Cu₂O [14] and about 934.9 eV which is related to copper ions from Cu²⁺ species. Moreover additional peak originating from Cu interaction with the hydroxyl groups of Al₂O₃ in the CuAl₂O₄ spinel compound [14] can be observed at about 936.2 eV. The possibility of the CuZnOx spinel formation was already observed in the literature [17]. However, we could exclude the possibility of the CuZnOx phase existence because its formation should also modify the XPS spectra in Zn 2p region. This is not the case in our study. Another alternative could be that this phase is formed in small amount, but in the mass of the catalyst. A satellite peak of Cu²⁺ is also detected at approximately 943 eV for all samples. However, its contribution varies depending on the quantity of Cu²⁺ species. This is in good correlation with data observed in the literature [18]. The peak at lowest binding energy at about 932.2 eV in all samples must be assigned to Cu⁰ + Cu⁺. In this case it is not possible to differentiate by XPS the proportion of those species (Cu⁰ or Cu⁺) are present on the catalyst surface. It is worth to note that the Cu⁰/Cu⁺ ratio could change after air exposure. Indeed, the Cu⁺ and Cu⁰ phases are not stable and could easily oxidize during transfer toward the XPS chamber. This is why we have decided to work with total Cu⁰ + Cu⁺ contribution instead of separate phases. In our experiments we used ex-situ reduction of our materials just before the XPS analysis took place. The transfer from the external reactor to the XPS chamber could modify the oxidation state of copper (Cu passivation due to the air exposure).

4. Discussion

4.1. Physical and chemical properties of the catalysts

As observed from the XPS and XRD results the pretreatment under hydrogen atmosphere induced changes in the oxidation state of the catalysts. CuO and CuAl₂O₄ are the only phases observed in XRD for calcined sample (fresh sample). Indeed, the large peak localized at 36° could be assigned to the overlapping peaks of these two species. No spinel phase CuAl₂O₄ was observed at 250 °C. As expected the formation of metal phase (and Cu⁺) is observed after hydrogen pretreatment at 350 °C. The small peak assigned to the spinel phase CuAl₂O₄, decreases significantly after the catalytic test with co-feed gases at 350 °C. On the contrary to that, the other phases (Cu₂O and Cu⁰) are principally observed after the catalytic test with co feed gases at 250 °C. In the case of CO₂, H₂ and H₂ + CO₂ gas promoters, the small fraction of Cu from spinel phase CuAl₂O₄ is also observed (Fig. 7b). Spinel phase has been suggested to be formed (17, 32). The fact that the small fraction of Cu spinel phase was observed by XRD and not by XPS, could be an indication that, this spinel phase is formed in a very low amount and probably in the mass of the catalyst. It could be concluded that after reduction pretreatment and catalytic test, in the presence of gas promoters, the catalyst is in more reduced state compared with the reduction pretreatment and test in absence of gas promoters. Gas promoters in the feed reduce copper. But oxidized copper is also observed. After reduction pretreatment and catalytic test at 350 °C metallic Cu (principally) and oxidizing Cu⁺ are the dominating phases. The reaction temperature and reducing atmosphere induce higher reduction state of the active phase.

The Cu 2p_{3/2} spectra in XPS for the spent catalyst after reaction with H₂, CO₂H₂ + CO₂ as co-feeds at 350 °C presents 3 peaks at

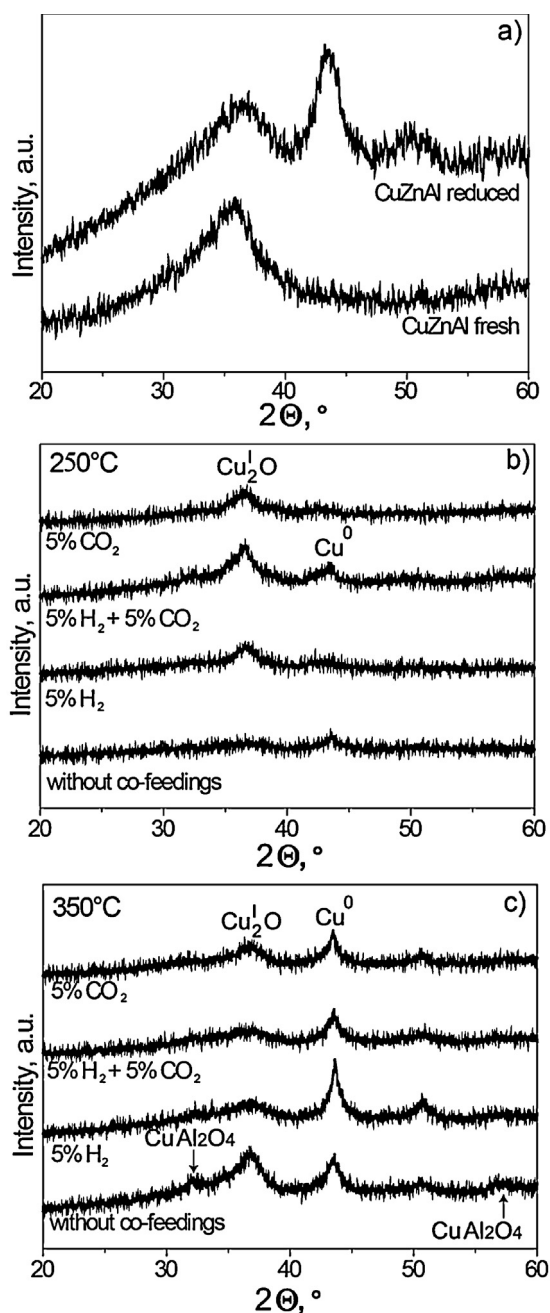


Fig. 7. XRD patterns of CuZnAl catalyst: A) fresh and reduced catalyst, B) spent catalyst in POMeOH at 250 °C and C) spent catalysts in POMeOH at 350 °C.

932.1–932.2, 934.2–935 and 936.2–936.6 eV corresponding to the $\text{Cu}^0 + \text{Cu}^+$, CuO and CuAl_2O_4 phases respectively. It corresponds well to the XRD results described above (Fig. 7c). It is recognized that both oxidation state and dispersion of active phase affect the selectivity to hydrogen in the POMeOH reaction. Thus, it can be concluded that the changes observed in the presence of gaseous co-feeds could be explained by changes affecting the oxidation state of Cu on the catalyst. Clearly the production of CO decreases when copper is reduced at its metallic state.

4.2. Comparison with thermodynamic calculations

The experimental trends for the H_2 selectivity for POMeOH in the presence of gaseous co-feeds respect to the POMeOH without co-feeds are opposite to those thermodynamically predicted

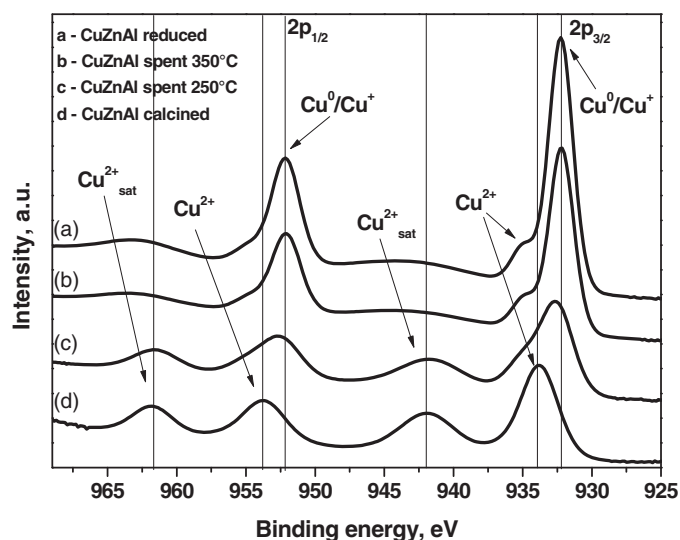


Fig. 8. XPS Cu2p region spectra for spent catalysts after Standard test (without gas co-feeding) at 250 °C and 350 °C.

for both, 250 °C and 350 °C. Thus, while selectivity to hydrogen increases in the presence of promoter gases, particularly in the presence of 5 vol% $\text{H}_2 + 5$ vol% CO_2 , thermodynamics predicts a decrease.

The selectivity to CO_2 decreases in the presence of dopes as predicted by thermodynamics at 250 °C and 350 °C, however such diminution is greater than that predicted, particularly in the case of using H_2 as promoter at 250 °C. Also, the selectivity to CO is very low or CO is not observed for POMeOH in the presence of dopes at both temperatures. Thermodynamic predicts an increase in the selectivity to CO when co-feeds are added to the feed.

These observations suggest that the system does not follow the trend that might be expected toward the new re-calculated values under the presence of dopes in the feed. These findings allows to conclude that the observed changes are not due to the changes suggested by the thermodynamics when promoter gases are added and might be interpreted by considering modifications in the physico-chemical properties of the catalysts, particularly in the kinetic of the reactions involved in POMeOH process.

4.3. Influence of the Cu oxidation state on catalytic activity and selectivity

CO could be produced via methanol decomposition or/and partial oxidation of methanol with low oxygen content or/and RWGS. In the case of reaction without dopes in the temperature range of 250–350 °C, hydrogen selectivity and methanol conversion increase with rising the temperature. It could be suggested that the CO formation was initiated at 250 °C by methanol decomposition, at which complete consumption of O_2 was observed. The high methanol conversion, H_2 selectivity and CO_2 selectivity at different reaction temperatures also confirm the involvement of steam reforming (SRM), water gas shift (WGS) and reverse water gas shift (RWGS) reactions under partial oxidation conditions.

Contrary to that, when the doping gases are added to the reaction flow (CO_2 or/and H_2) the CO formation decreases at 250 °C and 350 °C (H_2/CO increases), except for POMeOH + 5% CO_2 at 250 °C for which an increase in the CO formation is observed (H_2/CO decreases). This phenomenon fits well with the changes of Cu oxidation state. Indeed, as showed from XRD and XPS studies during the reaction with doping gases Cu is highly reduced. This is not the case after the standard POMeOH test (performed without dopes) where CuO or Cu^{2+} ions in spinel-type compound coexist with

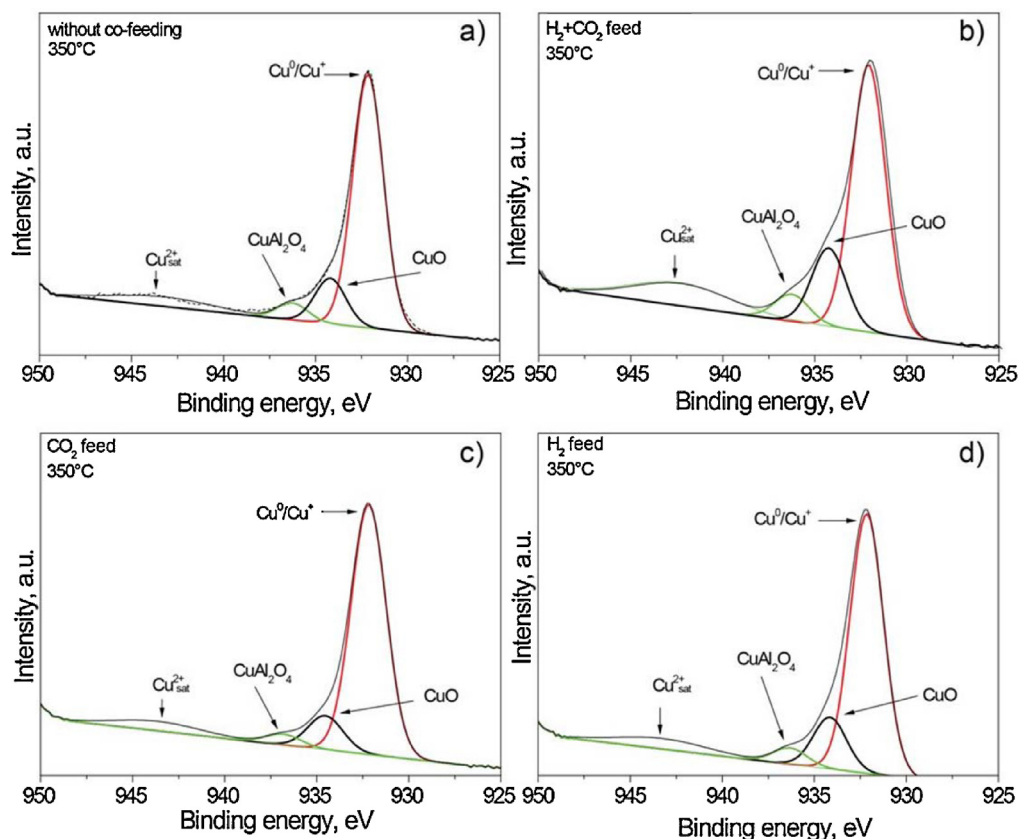


Fig. 9. XPS Cu 2p_{3/2} region for spent catalysts at 350 °C: a) catalytic test without gas co-feeding, b) catalytic test with H₂ + CO₂ feed, c) catalytic test with CO₂ feed and d) catalytic test with H₂ feed.

Cu⁰ and Cu¹₂O and for the reaction in the presence of 5% CO₂ at 250 °C for which Cu¹₂O is detected as the dominant phase by XRD and both a decrease in the Cu⁰/_(Zn+Al) and an increase in the Cu²⁺/Cu⁰/₊ ratios are observed by XPS. These results are in good concordance with the literature data. Indeed, partial oxidation of methanol over Cu [2,19–22] based catalysts has been recently studied for hydrogen production. It was shown that both Cu⁰ and Cu⁺ species are essential for hydrogen generation from methanol and the activity of catalyst is dependent on the ratio of Cu⁺/Cu⁰ in the catalyst [23,24]. Moreover, it was found that the catalytic activity is directly related to the copper metal surface area [21]. It could be suggested that the copper metal is active for partial oxidation of methanol to H₂ and CO₂, whereas Cu⁺ favors the formation of H₂O and CO and Cu²⁺ as CuO shows very low activity for methanol conversion producing only CO₂ and H₂O [25]. The importance of the initial state of oxidation of the catalyst have been studied and found that the temperature at which the reaction starts was shifted to higher values, when the degree of surface oxidation increased. Studies with Cu/ZnO/Al₂O₃ in oxidized, reduced and reduced + air-exposed samples have been performed. It was showed that Cu⁰ is an active species for higher activity, but Cu⁺ inhibits the POMEH to H₂ [26]. On the other hand, the appropriate introduction of Zn enhanced the Cu⁰ dispersion, which resulted in higher activity for H₂ production. However, over loading of Zn resulted in the formation of bigger crystallites of Cu₂O which decreases the activity of the catalyst [26].

Results strongly suggest that activity of the catalyst in partial oxidation of methanol may be related to its ability to stabilize adequate oxidation state of copper species. As shown on Fig. 10 a and b, the selectivity toward hydrogen depends on the concentration of Cu⁰/Cu⁺ phase and it increases when the concentration of Cu⁰ increases. It has been suggested in the literature that both Cu⁰ and

Cu⁺ species are essential for hydrogen generation from methanol and the activity of catalyst is dependent on the ratio of Cu⁺/Cu⁰ in the catalyst. Moreover, it was shown that complete oxidation of copper to Cu(II) renders the catalyst inactive for H₂ production, instead promoting methanol combustion. Our results show that a high concentration of Cu⁰ inhibits the CO formation. As Cu⁺ facilitates the formation of CO and H₂O, it could be suggested that the key point to produce hydrogen in absence of CO is the reduction of copper toward metallic state. Clearly the metallic state of copper promote the reaction 3 (WGS) inhibiting the reverse (RWGS), explaining the drastic decreases in CO formation. These results are also in line with recent results presented in the literature. Recently, the role of the oxidation states of Cu on the mechanisms of methanol decomposition, methanol oxidation and methanol steam reforming on a CuO (1 1 1) surface was studied theoretically [12,13]. It was demonstrated that the oxygen-precovered CuO (1 1 1) modifies the pathway of the reaction modifying the activation barrier of O–H bond-cleavage respect to the C–O bond cleavage, indicating, that oxygen acts on the surface of CuO(111) as a promoter for the formation of CH₃O by CH₃OH decomposition, confirming the fact that the oxidation state of copper is a crucial parameter to modulate the catalytic reactions on the surface.

The so-called “oxidative poisoning” however, was completely reversible [8]. At high methanol conversions during POMEH, all O₂ has been converted and the reaction mixture is reductive. Thereby, copper may again be transformed into its metallic state, which is active for H₂ production.

4.4. Control of the H₂/CO ratio

In the presence of co-feeds at 250 °C, the H₂/CO ratio strongly decreases or becomes very high (no CO was observed) in all cases

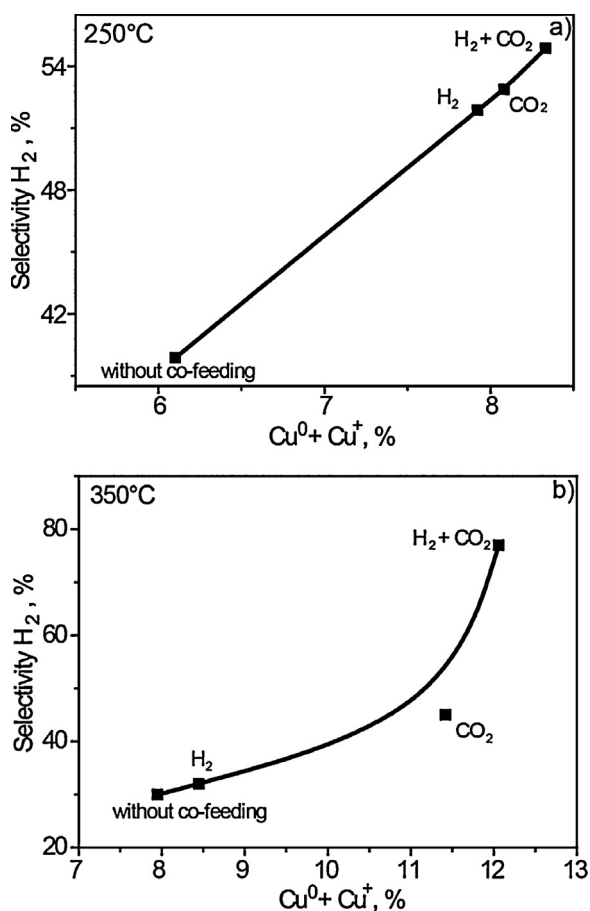


Fig. 10. Selectivity toward H₂ versus molar concentration of Cu⁰ + Cu⁺ as determined by XPS for catalysts without and with co-feedings. a) catalysts spent at 250 °C and b) catalysts spent at 350 °C.

as compared to the standard test (Table 1). A slight increase (from 1.3 to 1.7 or 2.2) is observed at 350 °C after co-feeding CO₂ or H₂. Interestingly, no CO production (no CO was observed) is presented for POMeOH + 5 vol % CO₂ + 5 vol % H₂ test at both temperatures. The most active catalyst which presented no CO production (no CO was observed) at 250 °C and 350 °C (95% or 100% conversion), has the higher Cu⁰ + Cu⁺ concentration (Table 3: 8.26 and 12.06 at 250 °C and 350 °C respectively) and significantly the higher proportion of Cu^{0/+} (Table 2: 2.21 and 3.31 at 250 °C and 350 °C respectively).

This confirmed the suggestion mentioned above that the higher reduction of copper is crucial to reduce the formation of CO. Cu^{0/+}/Cu_{total} ratio increases after the test with both, CO₂ and H₂, co-feeds in respect to the standard POMeOH. This increase is accompanied by a simultaneous increase in the H₂/CO₂ ratio. This would show that the increase in the Cu^{0/+}/Cu_{total} ratio is mainly due to the increase in the amount of surface Cu^{0/+} which would favor the H₂ and CO₂ production instead of CO formation. On the other hand, it has been indicated that Cu⁺ favors the formation of CO [25], then allowing us to conclude that in the partial oxidation of methanol the highly pure hydrogen (no CO is observed) can be obtained only when the full reduction of copper is favored, namely when copper is present in a metallic state.

Figs. 2–4, seems to indicate that the addition of H₂ and CO₂ leads to change of the H₂/CO atomic ratio but simultaneously reducing their production. We have discussed previously that the change in the H₂/CO atomic ratio is related with the oxidation state of copper on the surface. The fact that the production is also reduced means that the selective operation giving a low CO yield leads also to a reduction of the conversion and the yields of the other products of

the partial oxidation, confirming the fact that the oxidation state of copper (adequate Cu^{0/+}/Cu_{total} ratio) is crucial to modulate the low CO/H₂ atomic ratio. As the conditions of low CO production is related to a low yield of products it can be concluded that the number of copper atoms having the adequate oxidation state leading to a low CO/H₂ atomic ratio is not high. Any gap from this optimal oxidation state will increase not only the production but simultaneously the CO/H₂ atomic ratio, namely when the production increases, the selectivity in CO increases decreasing the selectivity in H₂. This can help to understand the difficulties to decrease the CO/H₂ atomic ratio using only solid dopes and/or operational reaction conditions, confirming the benefit or the necessity of use also gases dopes. A low production with a low CO/H₂ atomic ratio it is not a difficulty. Our study shows that, under the reaction conditions studied, this ratio can be modulated introducing gas dopes. Practically, a higher production, having a low CO/H₂ atomic ratio, could be obtained changing (more precisely, optimizing) the composition of the catalysts, the nature of solid dopes, the concentration of the gas dopes and the operational reaction conditions of the reaction (space velocity, concentration, temperature, etc.).

On the other hand the carbon balance in the reaction becomes low when the production is low. Under the sensibility detection conditions used in our analysis method, no other products were detected. The experimental error in the analysis of products can be estimated to 3%. The loss of carbon balance when production is low, could be attributed to coke formation. However by XPS, the presence of carbon was detected over all samples. The amount of carbon was low and stable among the various samples, thus indicating that there was no preferential coke deposition on the surface of the catalyst during the tests. One possibility is that at low production conditions there is formation of another products, other than, CO, CO₂, formaldehyde, methylformate non detected by the analysis method used.

4.5. Possible phases cooperation in POMeOH

Some authors described a “synergy” effect between the Cu and second metal oxide such as ZrO₂ [27,28]. Higher activity in this case was attributed to the stabilization of Cu₂O on the surface of the reduced catalysts or during the reaction [29,30]. It is believed that the formation of Cu₂O leads to both more active and more stable catalysts, since Cu₂O is less susceptible to sintering compared to the Cu metal [29,30]. Some authors claimed that formation of CuAl₂O₄ spinel could stabilize Cu active phase. It may be presumed, that when starting from a CuAl₂O₄ phase a better dispersion of the supported oxide (Cu₂O) could be obtain with a rather high thermal and mechanical stability of the catalysts [31]. In our case it is shown that the spinel CuAl₂O₄ phase disappears after reduction pretreatment and catalytic tests in absence or presence of co-feed gases, suggesting that this phase is not active in this reaction. In the case of CuO/ZnO mixed oxides the synergy effect between Cu and Zn was observed. Zn seems to influence the dispersion of Cu on the surface and also stabilize Cu⁺ active phase.

Activity of the Cu catalysts in oxidation of methanol could be also enhanced by doping the catalyst with Mn cations. It was shown that CuMnZn catalyst with the structure of copper–manganese spinel CuMn₂O₄ enhanced the turnover frequency (TOF) for methanol conversion at a lower temperature (from 4.2 to 10.1 s^{−1} at 150 °C) as compared to the Mn-free catalyst. It was also demonstrated that Mn played a role in electronic charge transfer, which enhances the formate decomposition [32].

Some authors claimed the leading role of Zn in spillover phenomena and also in the processes of Cu reduction, which occurs at lower temperature in the presence of ZnO [33]. Moreover, Cu⁺ species have also been observed in CeO₂-containing Cu catalysts [34,35] and isolated Cu²⁺ in lattice sites or in surface sites forming

a nano-sized two-dimensional structure [36]. It was observed that the addition of CeO₂ to Cu/Al₂O₃ catalysts increased methanol conversion, decreased CO selectivity and increased catalyst stability [37,38]. A synergy between separated phases, Cu⁰ and ZnO or Al₂O₃ (or both) cannot be completely excluded in our case. In fact it has been demonstrated in the hydrogenation of CO₂ to methanol, that the most active catalysts are formed when metallic copper (Cu⁰) is in close contact with ZnO. ZnO seems to promote the reduction of copper. The tendency of the catalytic system (CuZnO) is to segregate two phases: Cu⁰ and ZnO. A catalyst prepared by a mechanical mixing Cu⁰ and ZnO phases prepared separately, shown an important catalytic synergy in methanol formation [39]. Synergy is observed also when CuO/SiO₂ and ZnO/SiO₂ are put in contact. The synergistic effect was explained to H spillover across SiO₂ surface [40]. The cooperative effect between Cu⁰ and ZnO also seems to operate in the case of RWGS reaction, since the formation of CO was also enhanced when Cu⁰ and ZnO were present in mechanical mixtures but was negligible when pure Cu⁰ or ZnO were used. In the present case further experiments are needed to confirm or not this synergy between copper and zinc oxide. In the case of Cu/ZnO/ZrO₂ catalysts in the steam reforming of methanol reaction was observed that the Cu dispersion and catalyst composition strongly affected the catalytic performance of the materials. The increase in Cu particle size caused the deactivation of the catalyst. Moreover, the crystalline size of Cu was affected by the pretreatment conditions. In general, a higher calcination temperature (350 °C) and lower reduction temperature (250 °C) leads to a smaller crystalline size of Cu [41].

5. Conclusions

The co-feeding with H₂, CO₂ or H₂ + CO₂ modifies the oxidation state and the dispersion of copper. It could be concluded that the performances in the partial oxidation of methanol are the result of a complex scheme of reactions tuned by the number and nature of active sites able to catalyze the different reactions. The results confirm the very important role of the reaction products as co-feedings. Taking into account all results one could conclude that it seems to be possible to modulate the selectivity of the catalysts by controlling the oxidation state of Cu on the surface. This can be done by using doping gases instead of stoichiometric CH₃OH/O₂ composition and/or adding metallic promoters. The additional presence of CO₂ or/and H₂ in the reaction flow permits to stabilize Cu in a reduced state. It is concluded that the formation of metallic copper prevents (or/and decrease) the formation of CO allowing to obtain a highly pure hydrogen. The formation of spinel CuAl₂O₄ phase was also observed, but in minor amount. This spinel phase seems to be inactive in POMEH process.

References

- [1] J. Agrell, H. Birgersson, M. Boutonnet, J. Power Sources 106 (2002) 249–257.
- [2] J. Agrell, K. Hasselbo, K. Jansson, S.G. Jaras, M. Boutonnet, Appl. Catal. A: Gen. 2011 (2001) 239–250.
- [3] C. Mateos-Pedrero, S.R. González-Carrazán, M.A. Soria, P. Ruiz, Catal. Today 203 (2013) 158–162.
- [4] W. Gu, J.-P. Shen, Ch. Song, Prepr. Pap. -Am. Chem. Soc. -Div. Fuel Chem. 48 (2003) 804–807.
- [5] J. Agrell, H. Birgersson, M. Boutonnet, I. Melián-Cabrera, R.M. Navarro, J.L.G. Fierro, J. Catal. 219 (2003) 389–403.
- [6] J. Larminie, A. Dicks, Fuel Cell Systems Explained, Wiley, New York, 2000.
- [7] C. Mateos-Pedrero, S. Duquesne, S.R. González-Carrazán, M.A. Soria, P. Ruiz, Appl. Catal. A: Gen. 394 (2011) 245–256.
- [8] Y.L. Bi, K.J. Zhen, R.X. Valenzuela, M.J. Jia, V. Cortés Corberan, Catal. Today 61 (2000) 369–375.
- [9] E. Xue, J.R.H. Ross, R. Mallada, M. Menendez, J. Santamaria, J. Perregard, P.E. Hojlund Nielsen, Appl. Catal. A: Gen. 210 (2001) 271–274.
- [10] F. Dury, E.M. Gaigneaux, P. Ruiz, Appl. Catal. A: Gen. 242 (2003) 187–203.
- [11] F. Dury, M.A. Centeno, E.M. Gaigneaux, P. Ruiz, Catal. Today 81 (2003) 95–105.
- [12] Z.J. Zuo, L. Wang, P.D. Han, W. Huang, Int. J. Hydrogen Energy 39 (4) (2014) 1664–1679.
- [13] S. Sun, Y. Wang, Q. Wang, Appl. Surf. Sci. 313 (15) (2014) 777–783.
- [14] From NIST X-ray Photoelectron Spectroscopy Database, <http://nistdata.nist.gov/xps/>
- [15] Y. Lu, Y. Liu, S. Shen, J. Catal. 177 (1998) 386.
- [16] From The International Centre for Diffraction Data, File 1–1153 ICDD, <http://www.icdd.com/>
- [17] V.V. Pelipenko, D.I. Kochubey, A.A. Khassin, T.M. Yurieva React, Kinet. Catal. Lett. 86 (2005) 307–314.
- [18] D.A. Svintsitskiy, T.Y. Kardash, O.A. Stonkus, E.M. Slavinskaya, A.I. Stadnichenko, S.V. Koscheev, A.P. Chupakhin, A.I. Boronin, J. Phys. Chem. C 117 (2013) 14588–14599.
- [19] Y. Lin, L.T. Fan, S. Shafie, K.L. Hohn, B. Bertok, T.-J. Ferenc Friedler, Ind. Eng. Chem. Res. 47 (2008) 2523–2527.
- [20] Huang, S.-L. Chren, Appl. Catal. 40 (1988) 43.
- [21] L. Alejo, R. Lago, M.A. Peña, J.L.G. Fierro, Appl. Catal. A 162 (1997) 281.
- [22] S. Velu, K. Suzuki, T. Osaki, Catal. Lett. 62 (1999) 159.
- [23] I. Eswaramoorthi, V. Sundaramurthy, A.K. Dalai, Appl. Catal. A: Gen. 313 (2006) 22–34.
- [24] T.-J. Huang, S.-W. Wang, Appl. Catal. 24 (1986) 287.
- [25] R.M. Navarro, M.A. Peña, J.L.G. Fierro, J. Catal. 212 (2002) 112.
- [26] Z. Wang, W. Wang, G. Lu, Int. J. Hydrogen Energy 28 (2003) 151.
- [27] R. Pérez-Hernández, D. Mendoza-Anaya, A. Gutiérrez Martínez and A. Gómez-Cortés, in Catalytic Steam Reforming of Methanol to Produce Hydrogen on Supported Metal Catalysts INTECH Open Science, 2012, DOI: 10.5772/49965.
- [28] J.P. Breen, J.R.H. Ross, Catal. Today 51 (1999) 521–533.
- [29] H.T. Oguchi, T. Nishiguchi, H. Matsumoto, K. Kanai, Y. Utani, Y. Matsumura, S. Imamura, Appl. Catal. A Gen. 281 (2005) 69–73.
- [30] H. Oguchi, H. Kanai, K. Utani, Y. Matsumura, S. Imamura, Appl. Catal. A 293 (2005) 64–70.
- [31] G. Ertl, R. Hierl, H. Knozinger, N. Thiele, H.P. Urbach Appl. Surf. Sci. 5 (1980) 49–64.
- [32] K.Y. Lee, Y.J. ChCh. Shen, Huang, Ind. Eng. Chem. Res. 53 (2014) 12622–12630.
- [33] L.H. Castricum, H. Bakker, B. van der Linden, E.K. Poels, J. Phys. Chem. B 105 (2001) 7928–7937.
- [34] W.H. Cheng, J.S. Chen, J.-S. Liou, S.-S. Lin, Top. Catal. 22 (2003) 225–233.
- [35] Y. Liu, T. Hayakawa, K. Suzuki, S. Hamakawa, Catal. Commun. 2 (2001) 195–200.
- [36] R. Pérez-Hernández, A. Gutiérrez-Martínez, C.E. Gutiérrez-Wing, Int. J. Hydrogen Energy 32 (2007) 2888–2894.
- [37] X. Zhang, P. Shi, J. Mol. Catal. A: Chem. 194 (2003) 99–105.
- [38] F. Tonelli, O. Gorri, L. Arrúa, M.C. Abello, Quim. Nova 34 (2011) 1334–1338.
- [39] A. Karelavic, A. Bargibant, C. Fernández, P. Ruiz, Catal. Today 197 (2012) 109–118.
- [40] R. Burch, R.J. Chappell, S.E. Golunski, Catal. Lett. 1 (1988) 439–443.
- [41] J.E. Park, S.D. Yim, Ch S. Kim, E.D. Park, J. Hydrogen Energy 39 (2 (22) (2014) 11517–11527.